

Hydrogen Incorporation in Boron-Doped 6H-SiC CVD Epilayers Produced Using Site-Competition Epitaxy

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We report on the initial investigations of using site-competition epitaxy to control boron incorporation in chemical vapor deposition (CVD) 6H-SiC epilayers. Also reported herein is the detection of hydrogen in boron-doped CVD SiC epilayers and hydrogen-passivation of the boron-acceptors. Results from low temperature photoluminescence (LTPL) spectroscopy indicate that the hydrogen content increased as the capacitance-voltage (C-V) measured net hole concentration increased. Secondary ion mass spectrometry (SIMS) analysis revealed that the boron and the hydrogen incorporation both increased as the Si/C ratio was sequentially decreased within the CVD reactor during epilayer growth. Epilayers that were annealed at 1700°C in argon no longer exhibited hydrogen-related LTPL lines, and subsequent SIMS analysis confirmed the outdiffusion of hydrogen from the boron-doped SiC epilayers. The C-V measured net hole concentration increased more than threefold as a result of the 1700°C anneal, which is consistent with hydrogen passivation of the boron-acceptors. However, boron related LTPL lines were not observed before or after the 1700°C anneal.

Key words: Boron, hydrogen passivation, silicon carbide, site-competition epitaxy

INTRODUCTION

The intrinsic material advantages of silicon carbide are currently being exploited in the development of high power and high frequency semiconductor devices for service in high temperature, corrosive, and high radiation environments. These microelectronic devices include high voltage Schottky rectifiers and power metal-oxide semiconductor field-effect transistors (MOSFETs),¹ microwave and millimeter-wave devices,^{2,3} and high temperature, radiation resistant junction field-effect transistors (JFETs).⁴ However, in order for the theoretically calculated advantages^{1,5} of using SiC to be fully realized, advancements are needed both in the bulk growth and in the epilayer growth of SiC. For example, improvements in the bulk growth of SiC are needed for elimination of

device limiting micropores and micropipes.⁶ Other advancements are needed in the epilayer growth process. In particular, dopant incorporation during the growth of SiC epilayers must be understood and reliably controlled. Site-competition epitaxy, for example, is a recent advancement for the control of dopant incorporation for both aluminum (p-type) and nitrogen (n-type) doped epilayers, which has resulted in increased doping range and improved doping reproducibility for the growth of chemical vapor deposition (CVD) SiC epilayers.⁷ Use of site-competition epitaxy has led to improved device performance which includes high voltage diodes,⁸ ohmic as-deposited contacts,⁹ and high temperature JFETs.¹⁰

The usefulness of site-competition epitaxy relies upon each particular dopant atom substituting only for either a Si atom in the Si-site or for a C atom in the C-site of the growing SiC epilayer. Site-competition epitaxy has been successfully used for control of both

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Al and N doping, partly because Al substitutes for Si in the Si-sites whereas N substitutes for C in the C-sites of the SiC lattice.¹¹ In contrast, boron has been reported as an amphoteric p-type dopant in SiC, substituting into both the C-site and into the Si-site of the SiC lattice.^{11,12}

In this paper, we report on the initial investigations of using site-competition epitaxy to control boron incorporation in CVD 6H-SiC epilayers. Also reported herein is the detection of hydrogen in boron-doped CVD SiC epilayers and hydrogen-passivation of the boron-acceptors. Hydrogen has been previously detected both in ion implanted,^{13,14} and in CVD grown SiC epilayers.¹⁵ However, we report a correlation of hydrogen concentration contained in CVD grown 6H-SiC epilayers with the amount of boron incorporated during the epilayer growth process. Both the site occupancy and hydrogen incorporation are aspects of boron-doped SiC epilayers which could impact other studies, such as the investigations of potential reductions in interface states for improved MOS devices.^{16,17} Therefore, if boron does occupy both the C-site and Si-site, then control over site occupancy must first be accomplished before potential effects of site occupancy on resulting device properties can be accurately determined.

EXPERIMENTAL

The 6H-SiC epilayers were grown on commercially available n-type (0001)SiC Si-face boules-derived wafers¹⁸ in an atmospheric pressure CVD system,^{19,20} with a typical growth rate of 3–4 $\mu\text{m/h}$. The SiC substrates were pre-cleaned using a standard degreasing solution, followed by immersion in boiling sulfuric acid for 10 min, with a final deionized-water rinse and then dried with filtered nitrogen. The cleaned substrates were placed onto a SiC-coated graphite susceptor and then loaded into a water-cooled fused-silica reactor using a fused-silica-carrier. The samples were heated via the radio frequency (rf) coupled susceptor which was temperature controlled at 1450°C using an optical pyrometer. Silane (3% in H_2) and propane (3% in H_2) were used as the sources for SiC epilayer growth, whereas 3% hydrogen chloride gas in hydrogen was used during a 1350°C in situ 4 min etch just prior to epilayer growth. All gases were mass flow controlled, including the ultra-pure hydrogen carrier-gas which was purified by using a heated-palladium diffusion cell. The epilayers were doped p-type by the addition of diborane (100 ppm or 500 ppm B_2H_6 in H_2) into the reactor during epilayer growth.

The annealing experiments were carried out in a CVD-polycrystalline SiC cavity at 1700°C for 0.5 h in an atmospheric pressure, ultra-pure argon environment. Secondary ion mass spectrometry (SIMS) was performed²¹ using a CAMECA IMS-4f double-focusing, magnetic sector ion microanalyzer. Cesium bombardment was used for determination of hydrogen, boron, and nitrogen atomic concentration profiles by using the detector in a negative secondary ion detection mode to monitor (H)⁻ and the diatomic species

$\text{B}(\text{+C})$, $\text{N}(\text{+C})$, respectively. The aluminum and higher accuracy boron elemental concentrations were determined by using oxygen bombardment and a positive secondary ion detection mode. The sputter-time data was converted into depth data by measurement of crater depths, by using a stylus profilometer. Capacitance-voltage (C-V) measurements were obtained at 100 kHz on a mercury-probe instrument with a mercury-Schottky (contact area = $1.64 \times 10^{-3} \text{ cm}^2$), using the mechanical sample-hold-down paddle as the electrical ground on the back of the sample. The low temperature photoluminescence (LTPL) was performed at 2K by immersing the SiC samples in pumped liquid helium, and excited using the 3250Å radiation from a He-Cd laser. The LTPL spectra were recorded on a 0.75 meter Spex monochromator (10Å/mm), using a thermoelectrically cooled (-30°C) GaAs/CsO photomultiplier and a photon counting system.

RESULTS AND DISCUSSION

Boron Incorporation

The amount of boron incorporated into these 6H-SiC epilayers was controlled by using site-competition epitaxy. As previously reported,⁷ site-competition epitaxy is a dopant control technique based on appropriately adjusting the Si/C ratio within the growth reactor to effectively control the amount of dopant incorporated into substitutional SiC crystal lattice sites. These sites are either carbon-lattice-sites (C-sites) or silicon-lattice-sites (Si-sites) located on the active growth surface of the silicon carbide crystal. Nitrogen donor atoms are believed to occupy only the C-sites for densities below 10^{20} cm^{-3} whereas aluminum acceptor atoms occupy only the Si-sites in a SiC lattice.^{11,22} The model for site-competition epitaxy is based on the principle of competition between nitrogen and carbon for the C-sites and between aluminum and silicon for the Si-sites on the growing silicon carbide surface. For example, it was previously reported⁷ that the concentration of aluminum dopant atoms incorporated into a growing silicon carbide epilayer can be decreased by increasing the silane concentration so that Si out competes Al for the Si-sites. Conversely, the concentration of aluminum incorporated into a growing SiC epilayer can be greatly increased (i.e. for degenerate p-type epilayers) by decreasing only the Si/C ratio within the reactor during epilayer growth. The Si/C ratio can be decreased by either increasing the carbon-source concentration (i.e. by increasing the propane flow into the reactor) or by decreasing the silicon-source concentration in the CVD reactor during epilayer growth.

Therefore, in order to utilize this dopant control technique, it first must be determined whether the specific dopant atom occupies either the C-site or the Si-site of the SiC lattice. Boron has been reported to occupy both the Si-site and the C-site,^{11,12,23–25} which would preclude effective use of site-competition epitaxy for control of boron doping in SiC. However, our CVD experimental results indicate that boron prefer-

entially occupies the Si-site of the SiC lattice. We have found that boron incorporation into the SiC epilayer decreases as the silane concentration increases (i.e. increasing the Si/C ratio), which is consistent with the increased amount of silicon outcompeting the boron for available Si-sites during growth of the SiC epilayer.

Conversely, boron incorporation can be increased by decreasing the Si/C ratio by decreasing the silane concentration or, alternatively, increasing only the propane concentration. Varying only the propane concentration for effective control of the boron doping is illustrated in Fig. 1, in which the Si/C ratio was decreased stepwise during epilayer growth by successive increases in propane concentration while maintaining a constant silane and diborane concentration. Here, the boron incorporation in the epilayer increases as the propane concentration is increased because of the relative decrease in the Si/C ratio within the growth reactor. This relative decrease in silicon concentration enables the boron atoms to out compete the silicon atoms for more of the available Si-sites on the surface of the growing SiC epilayer, resulting in increased boron incorporation into the SiC epilayer.

To determine the reproducibility of the doping control, numerous boron-doped SiC epilayers were grown during separate 2 h growth experiments, each using a constant Si/C ratio ranging from Si/C = 0.1–0.5. For selected epilayers, SIMS determined elemental boron concentration was compared to the net carrier concentration measured using mercury-probe C-V. A typical epilayer grown using a Si/C = 0.51 had a C-V measured net carrier concentration of $p = 5 \times 10^{15} \text{ cm}^{-3}$ as compared to a net carrier concentration of $p = 3.5 \times 10^{17} \text{ cm}^{-3}$ for an epilayer grown using a Si/C = 0.11 in a separate experiment but with an identical diborane concentration (1.6 ppm). Secondary ion mass spectroscopy analysis revealed an elemental boron

concentration of $[B] = 6.5 \times 10^{16} \text{ cm}^{-3}$ for the lower doped ($p = 5 \times 10^{15} \text{ cm}^{-3}$) epilayer and a $[B] = 1 \times 10^{18} \text{ cm}^{-3}$ for the more highly boron-doped ($p = 3.5 \times 10^{17} \text{ cm}^{-3}$) SiC epilayer. The large increase in boron incorporation resulting solely from a change in the Si/C ratio illustrates

- the strong dependency of the boron incorporation on the Si/C ratio used during epilayer growth, and
- the preferential B occupancy of the Si-site vs the C-site.²⁶

Low Temperature Photoluminescence Identification of Hydrogen

Three boron-doped SiC epilayers, grown using identical Si/C ratios but with different diborane concen-

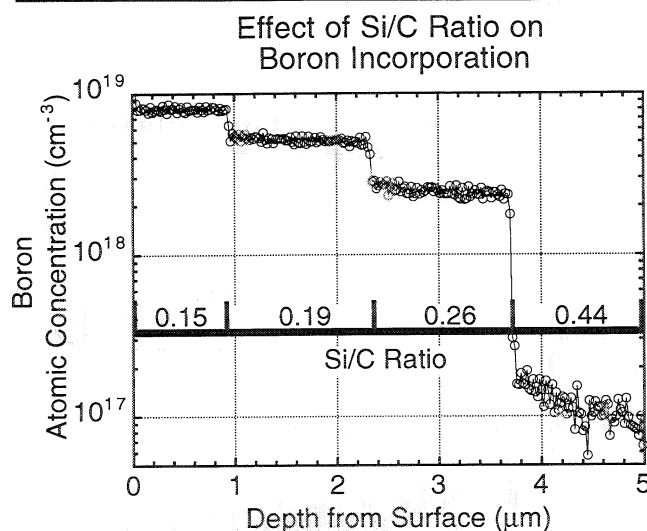


Fig. 1. The SIMS determined atomic boron concentration increased as the Si/C ratio was decreased by changing only the propane flow (from 450 to 1350 ppm) while maintaining a constant silane (200 ppm) and diborane (3 ppm) flow during the CVD 6H-SiC epilayer growth.

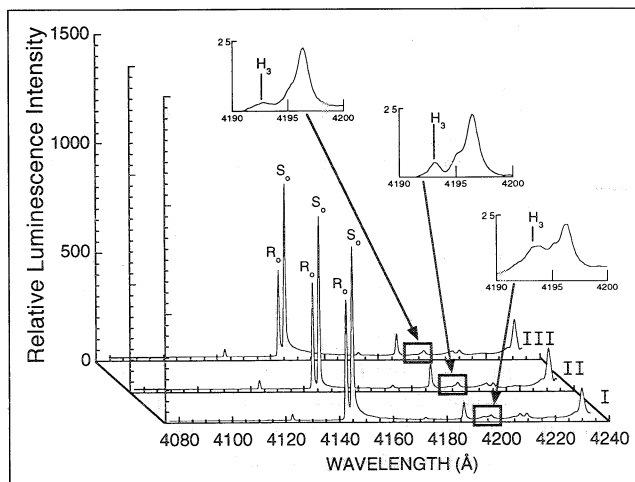
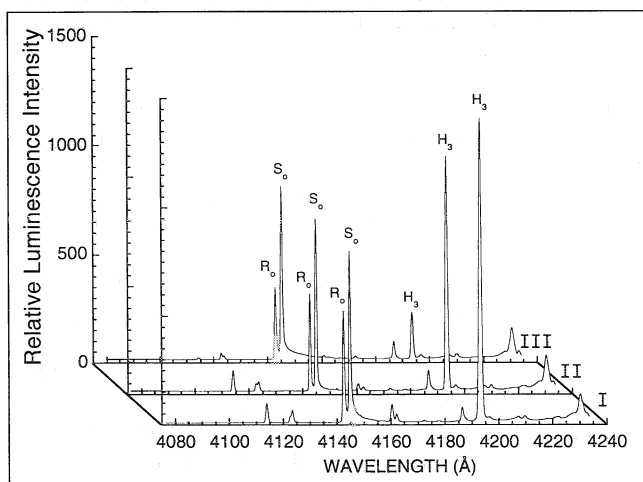


Fig. 2. (a) Low temperature photoluminescence spectra of three 6H-SiC epilayers before anneal, with decreasing hydrogen-related line intensities (labeled H_3). Corresponding to the decrease in H_3 line intensities, the samples had decreasing measured net carrier concentrations of I) $p = 2 \times 10^{16} \text{ cm}^{-3}$, II) $7 \times 10^{15} \text{ cm}^{-3}$, and III) $2 \times 10^{15} \text{ cm}^{-3}$. The LTPL spectra were normalized relative to the intensity of S_0 , one of the nitrogen bound exciton LTPL lines. (b) LTPL spectroscopy of the samples after a 1700°C anneal in argon for 0.5 h revealed a relative decrease in the intensity of the hydrogen related line (labeled H_3). The insets of the LTPL spectra from 4190 to 4200 Å illustrate that a small amount of hydrogen remained in the epilayers following the high temperature anneal.

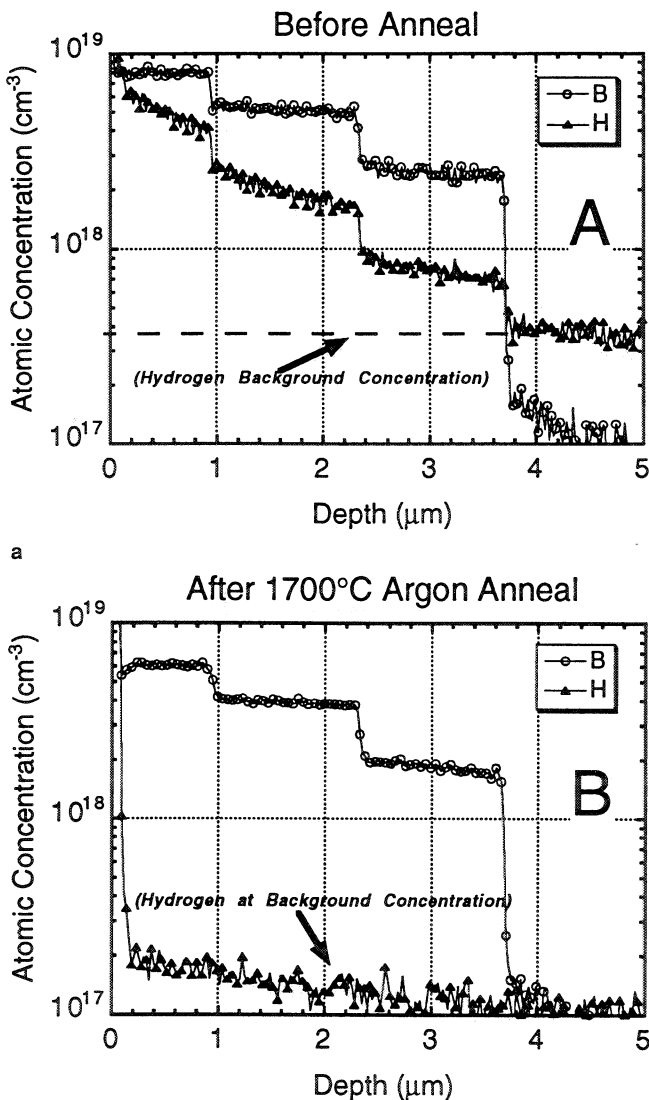


Fig. 3. (a) Secondary ion mass spectroscopy analysis of a boron-doped epilayer revealed that prior to anneal the hydrogen concentration increased as the boron concentration increased within the CVD SiC epilayer. (b) SIMS analysis after an anneal in argon at 1700°C (0.5 h) revealed that the hydrogen concentration is at or below the H₂ detection limit of the SIMS instrument, indicating the outdiffusion of hydrogen during the high temperature anneal. Also, no significant solid state diffusion of boron was detected, as evidenced by the continued sharpness of the boron concentration profile.

trations, were subsequently examined using low temperature photoluminescence spectroscopy (LTPL). Identical Si/C ratios were used in order to eliminate potential effects of different propane concentrations on hydrogen incorporation, thereby isolating the hydrogen incorporation effect to only the change in diborane concentration. The resulting spectra, shown in Fig. 2a, reveal that a significant amount of hydrogen was contained in each of the boron-doped epilayers. The most prominent line (at 4193Å and labeled H₃), observed both in hydrogen-ion implanted SiC^{13,14} and in CVD grown SiC epilayers,¹⁵ has been previously assigned to a hydrogen center. The H₃ line intensity increased, relative to the two nitrogen bound exciton

lines (S₀ and R₀), as the C-V net carrier concentration increased for the sample series $p = 2 \times 10^{15} \text{ cm}^{-3}$, $p = 7 \times 10^{15} \text{ cm}^{-3}$, and $p = 2 \times 10^{16} \text{ cm}^{-3}$. This correlation of increased H₃ intensity with increasing p-type character suggests that the hydrogen incorporation is directly proportional to the amount of boron incorporated into the SiC epilayer.

The intensity of all hydrogen related spectra decreases after the samples are subjected to a 1700°C anneal in argon for 0.5 h (see Fig. 2b). In comparing the results shown in Fig. 2b with those of Fig. 2a, it becomes evident that the H₃ line intensity has severely decreased relative to S₀, a nitrogen bound exciton line. This indicates that either most of the hydrogen has diffused out of the SiC epilayer or the optical activity of the hydrogen has been altered. Also note that lines related to the boron center in SiC were not observed before or after the high temperature anneal, which is less understood and still under investigation.

SIMS Analysis for H Incorporation

Epilayers containing stepped increases in boron concentration [B], from only varying the Si/C ratio, were prepared as described in Fig. 1 and subsequently analyzed for hydrogen using SIMS. This was done to

- confirm that hydrogen and boron incorporation are related, and
- determine whether the hydrogen was removed or if its optical activity was simply altered as a result of the 1700°C anneal.

The results of SIMS analysis of the [B]-stepped epilayer, prior to the high temperature anneal, are displayed in Fig. 3a. The increase in hydrogen concentration is observed to correspond with the increase in boron concentration within the epilayer. This indicates that the hydrogen incorporation is directly related to the boron incorporation in the 6H-SiC epilayers. We do not know whether the hydrogen atom is substitutional or defect related²⁷ as was previously reported for hydrogen in other semiconductor materials. (Note that the hydrogen concentration profile displayed in Fig. 3a is artificially less than the boron concentration and each step in the hydrogen concentration profile also contains a downward slope, both of which are artifacts of the SIMS measurement.)²⁸

After a 1700°C anneal for 0.5 h in argon, the sample was again SIMS depth profiled for determination of boron and hydrogen concentration. The results are displayed in Fig. 3b which indicates that the hydrogen has diffused out of the SiC epilayer as a result of the 1700°C anneal. The amount of hydrogen remaining within the boron-doped epilayer is below the hydrogen background concentration ($< 2 \times 10^{17} \text{ cm}^{-3}$) in the SIMS instrument. Also, it is interesting to note that boron does not undergo appreciable solid state diffusion as a result of the 1700°C anneal, which is evidenced by the continued sharpness of the [B]-profile displayed in Fig. 3b.

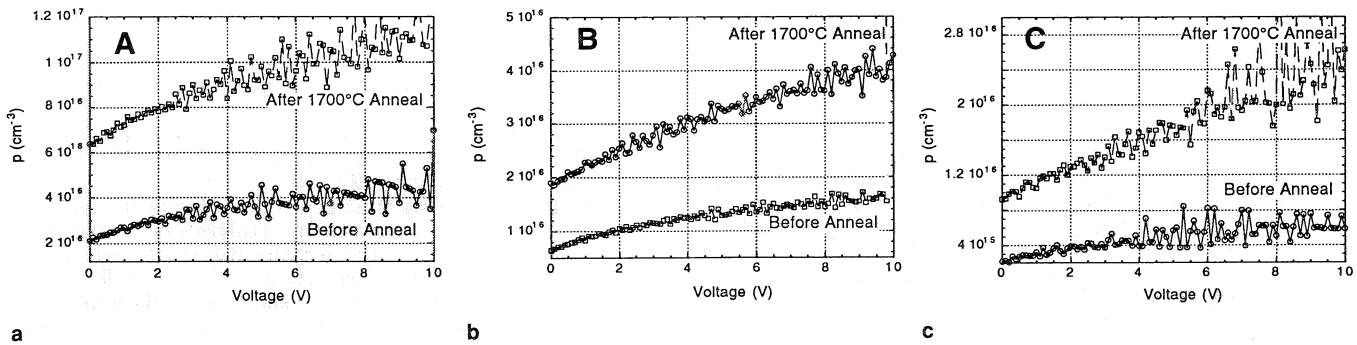


Fig. 4. The C-V measured net carrier concentrations before (lower plot in each graph) vs after (upper plot) a 1700°C anneal indicate more than a threefold increase in the net carrier concentration for all three doping levels. Identical Si/C ratios were used during the epilayer growth in order to minimize potential effects of different propane concentrations on hydrogen incorporation.

Hydrogen Passivation of Acceptors

To determine the extent of hydrogen passivation of dopants, the sample series discussed in Fig. 2 was examined using mercury-probe C-V before and after a high temperature anneal in argon. The C-V results after a 1700°C anneal, vs before the anneal, indicate a three to fourfold increase in the net carrier concentration for all three doping levels (see Fig. 4). This increase indicates that, prior to the anneal, hydrogen was passivating the acceptor atoms of the B-doped SiC epilayers. The amount of hydrogen-passivated acceptors was estimated for each sample by a comparison of the measured net carrier concentration (at $V = 0$) before and after the 1700°C anneal. The increase in carrier concentration, due to the reduction in hydrogen-passivation with post-anneal, was approximately 4.5X, 3X, and 3.25X for the three samples with post-anneal net carrier concentrations of $p = 9 \times 10^{15} \text{ cm}^{-3}$, $p = 1.9 \times 10^{16} \text{ cm}^{-3}$, and $p = 6.5 \times 10^{16} \text{ cm}^{-3}$, respectively.

SUMMARY

We have demonstrated that site-competition epitaxy is effective for the control of B-doping in CVD 6H-SiC(0001) epilayers, with B incorporation inversely proportional to the Si/C ratio used within the reactor during SiC epilayer growth. This is consistent with B substituting for Si in the Si-site, in agreement with previous ENDOR²⁹ and EPR¹² results. Both LTPL and SIMS analysis of the boron-doped epilayers indicate that the hydrogen concentration contained in the epilayers increased with increasing boron incorporation. The LTPL hydrogen related lines significantly decreased in intensity following a 1700°C anneal, which is consistent with the outdiffusion of hydrogen during the high temperature anneal. Secondary ion mass spectroscopy analysis of a boron-doped SiC epilayer provided additional evidence to support the removal of hydrogen as a result of the 1700°C anneal in argon. However, SIMS analysis did not reveal evidence for boron solid state diffusion for a sample containing a stepped boron concentration profile also annealed at 1700°C for 0.5 h. Mercury probe C-V measurements indicate that a significant amount of the boron acceptors were passivated by the hydrogen

incorporated into the epilayers, whereas no evidence for donor passivation was found.

Although previous work has also suggested that B occupancy in SiC may be amphoteric, our results indicate that there is at least a preference for B incorporation into the Si-site for boron-doped CVD epilayers. However, we are currently working to determine to what extent B incorporates into the C-site in CVD grown 6H-SiC epilayers.

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